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Fluctuation of dissolved heavy metal concentrations in the leachate from anaerobic digestion of municipal solid waste in commercial scale landfill bioreactors: the effect of pH and associated mechanisms

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Highlights

Homogenous substrate wetting was achieved using a unique flood and drain process

Eight heavy metals were profiled during commercial-scale digestion of MSW

Heavy metal concentrations were correlated to anaerobic degradation stages

pH was an indicator for determining relative values of dissolved heavy metals

Adsorption (Zn, Cu, Ni, Pb & Cd), complexation (Cr) or both (As & Co) affected metal distribution

Abstract

Heavy metals present in landfill leachate have infrequently been related to complete anaerobic degradation municipal solid waste (MSW) due to discrete ages of deposited MSW layers and leachate channelling in landfills. In this study, anaerobic digestion of MSW was performed in two enclosed 1000 tonne bioreactors using a unique flood and drain process. Leachates were characterised in terms of pH, soluble chemical oxygen demand, volatile fatty acids (VFAs), ammonium nitrogen and heavy metals over the entire course. All parameters, including the pH, fluctuated during acidogenesis, acetogenesis and methanogenesis, which strongly impacted on the dynamics of dissolved heavy metal concentrations. The simulation of dissolution and precipitation processes indicated that metal sulphide precipitation was not a factor as metal concentrations exceeded solubility limits. The correlation of pH and dissolved heavy metal concentrations indicated that other, or combinatorial, mechanisms were involved at the homogenisation conditions within the bioreactors. Besides the dissolution and precipitation process, the main processes most likely involved in metal distributions were adsorption (Zn, Cu, Ni, Pb and Cd), complexation (Cr) or combinations of both process (As and Co).

***Keywords*:** anaerobic digestion; flood and drain; heavy metal; landfill bioreactor; leachate; municipal solid waste

1. Introduction

Sanitary landfills remain as the predominant repository for municipal solid waste (MSW) worldwide. Nearly 42 % of the waste (~22.2 million tonnes) generated in Australia during 2009-2010 was disposed to landfills [1]. Water percolating through the waste interacts with organic and inorganic components to generate a leachate. Landfill leachate is of concern because it contains heavy metals or metalloids, organic contaminants (e.g., phenolic compounds) and pathogens at various strengths. These pose a serious environmental hazard to ground water and surface water if not properly managed and treated - especially with inevitably imperfect or damaged landfill liners during landfill construction [2]. Monitoring of heavy metal concentrations in landfill leachate has been prescribed by authorities and is routinely performed by landfill operators [3]. Heavy metal toxicity is a major concern and can also be assessed using biological assay [4, 5]. Landfill leachate composition varies due to waste composition, age (i.e., degree of decomposition) and soil characteristics, as well as local environmental conditions such as precipitation and ambient temperature [6]. The stability of MSW correlates to leachate quality in terms of heavy metals, ammonia and chemical oxygen demand (COD).

Physical, chemical and microbial processes all affect the heavy metal concentrations in landfill leachate. The accumulation and transport of heavy metals in a treatment system is primarily influenced by six mechanisms: (1) dissolution and precipitation, (2) sorption to extracellular biopolymers and wastewater/leachate particles [7], (3) bio-sorption to microbial cell walls [8], (4) complexation with dissolved organic matter (DOM), (5) bio-accumulation within microbial cells [9] and (6) microbial

activities such as sulfate reducing bacteria (SRB) producing H_2S [10].

A number of studies demonstrate the natural attenuation of heavy metals within a landfill. The majority of these studies present snapshots of heavy metal speciation in leachate with discrete ages from either operating or closed mature landfills [6, 11-16]. However, metal speciation and abundance are the net effect of layers of MSW deposited in landfills, ranging in stages of degradation. It is therefore difficult to relate the heavy metal concentration and species to any specific degradation stage within the landfill. Acidogenesis, acetogenesis and methanogenesis during anaerobic digestion of the organic fraction of MSW (OFMSW) impact on the pH in the leachate. The pH is one of the most significant contributing factors to metal speciation and distribution. Other factors that affect metal distribution in the soluble or insoluble phase include adsorption to particulates, complexation with DOM (e.g. humic acids) and the influence of biological activity (e.g., sulphate reducing bacteria). Although there have been many attempts to model these interactions and subsequent metal distributions, model simulations are hindered by insufficient certainty regarding solubility product constants [11]. Furthermore, few studies report on the fluctuation of dissolved heavy metal due to the interaction of multiple factors during anaerobic digestion in landfill bioreactors [17].

Clarke et al.[18] first demonstrated a flood and drain regime for degrading MSW large-scale using two in-ground bioreactors containing 1026t and 915t of shredded MSW (<8cm). The bioreactors, labelled for the purposes of this paper as LR1 and LR2, were flooded and drained repeatedly, to achieve an average methane yield of 211 ± 38 $Nm^3.t^{-1}VS$. The bioreactors were digested sequentially. The first bioreactor

(LR1) was flooded and drained 37 times over a period of 290 days, while the second bioreactor (LR2), using the mature leachate from the first bed, was flooded and drained 15 times over 104 days. Flooding homogenises conditions within a packed waste bed more than trickle flow (typically applied in landfills and landfill bioreactors), where fluid channelling may occur. Consequently, trends in dissolved metal concentrations from a flood and drain bioreactor can be more clearly related to a stage of degradation within the bioreactor, as opposed to a trickle flow bioreactor where leachate concentration trends are affected by the evolving and complex hydraulic behaviour within the waste bioreactor.

The flood and drain process intensified the biodegradation process, reflected by (1) high volatile fatty acids concentrations, (2) high methane production rates, and (3) shorter duration for stabilization of MSW. Therefore, the aims of this study were (1) to investigate the fluctuation of heavy metals in landfill bioreactors digesting shredded MSW in association with its biodegradation stages, and (2) to propose possible mechanisms for heavy metal distributions in landfill bioreactors.

2. Materials and methods

2.1 Landfill bioreactors

Details of landfill bioreactors design and the flood and drain operation are presented in Clarke et al [18]. Operation for bioreactors is briefly summarised here. The flood and drain operation was performed on two co-located landfill bioreactors (namely LR1 and LR2) that were loaded simultaneously with 1026 and 915 tonnes of the sub-8cm fraction of shredded mixed MSW. A third reactor cell served solely as a reservoir for leachate used to flood LR1 and then LR2. The MSW in LR1 was digested first (in

isolation) by flooding and draining once weekly (to avoid excessive souring), until gas production had declined to a steady residual level. LR2 was flooded and drained for the first time (186 days after the first flood and drain of LR1), using the same inventory of leachate from LR1. Each bioreactor was then flooded and drained twice per week for the remaining 104 days. The initial heavy metal concentrations in the leachate reservoir for the sequential flooding and draining operation in both reactors is shown in Table 1.

2.2 Leachate analysis

Analytical methods for measuring pH, soluble chemical oxygen demand (sCOD), volatile fatty acids (VFAs), and total ammonium-N are described in Clarke et al. [18]. Leachate samples were filtered through 0.45 µm filters (PES Millipore) to remove solids, and the supernatant was analysed for pH (TPS, Springwood, Australia), sCOD, VFAs, total ammonium-N and dissolved heavy metal concentrations. sCOD was measured according to Standard Methods (APHA, 1998) using a Thermoreactor TR 300 (Merck, Germany) and an SQ 118 Photometer (Merck, Germany). VFAs were determined by gas chromatography (Agilent Technologies 7890A, USA) using a flame ionisation detector (FID) and a polar capillary column (DB-FFAP) after dilution and addition of an internal standard (1000 ppm stock of six VFAs) and 1% formic acid. Total ammonium-N was analysed on a Flow Injection Analyzer (Lachat QuikChem8000, USA).

Total metal ion concentrations for Zn, Cu, Pb, Cr, As, Cd, Co and Ni were analysed by inductively-coupled plasma optical emission spectrophotometer (ICP-OES, Perkin Elmer Optima 7300DV, USA) after digestion the filtered leachate with nitric acid. The

digestion was done in a MARS Xpress microwave with Teflon tubes. The detection limits range between 1 to 10ppb, depending on the element and sample composition. Nitric acid (5mL) was added to sample (5mL) to make a total volume of 10mL. Samples were mixed and then digested in the MARS Xpress microwave in Teflon tubes for 10 minutes at 160℃ and then 10 minutes at 170℃. The sample tube was allowed to cool and the liquid was transferred to a 10mL tube. The samples were diluted to a final nitric acid concentration of 5%, mixed and analysed on the ICP-OES. It is anticipated that heavy metals in dissolved fraction (<0.001 µm) and colloidal fraction with smaller size (between 0.001 – 0.45 µm) were analysed [19].

2.3 Establishment of PHREEQC simulation for the heavy metal concentrations

The geochemical modelling package PHREEQC Version 2 was used to model the heavy metal concentrations in landfill cell leachate at equilibrium. It is capable of describing chemical reactions based on the chemistry of aqueous solutions in equilibrium with other components, such as minerals, gases, solid solutions, and adsorptive surfaces. Thermodynamic data was obtained from the Lawrence Livermore National Library database [20].

The metal concentration profiles in both reactors were modelled to assess whether solubility constraints of selected metal salts control the dissolved concentration of each heavy metal during the entire anaerobic digestion. The simulations were

restricted to equilibrium conditions and therefore did not take into account the rate at which precipitation and dissolution reactions would occur to approach equilibrium with respect to these constraints. The inputs were total dissolved elemental concentrations present in the leachate sample on the entire digestion period for LR2. Other model inputs included (1) temperature and pH, (2) an initial reducing environment (pE: 3.1),based on the redox potential of -183 mV [21], (3) total sulphur concentration, (4) inorganic carbon concentration in solution based on the temperature and CO_2 partial pressure in the landfill bioreactor, (5) selected mineralogical phases, and (6) a charge balance using chloride. Metal hydroxide, metal carbonate and metal sulphide were selected as model mineralogical complexes. For modelling purposes, the acetate concentration, based on the COD equivalent of total VFAs was used as a parameter [20]. The pH measured in each leachate sample was adopted for each simulation. Updated log *K* values for Chromium (III) species were used in this study, which can be found in the supplementary materials of other studies [22, 23]. All other equilibrium constants are included in the standard PHREEQC database [24]. PHREEQC was then used to predict equilibrium concentrations for the dissolved heavy metals in the leachate. The effect of bio-sorption, bio-accumulation, physical sorption and metal-DOM complexation wasn't incorporated into the simulation due to the lack of available input information (e.g., values for binding parameters by complexation).

3. Results and discussion

3.1 Change in leachate pH, COD, VFA and NH_4-N content

The general characteristics of leachate in terms of pH, temperature, COD, VFA and NH_4-N (Fig. 1) are described in Clarke et al. [18]. Briefly, the increase from an initial

pH of 6.64 to 7.94 (Day 81) in LR1 coincided with a dramatic decrease in VFA concentrations and a large increase in methane production rate to ~39 m^3 CH_4 h^{-1} (Day 81) during this period, with a peak methane production rate of ~78 m^3 CH_4 h^{-1} on Day 91. Thereafter, the pH in the LR1 remained steady (~7.9) until LR1 was sequenced with LR2 (Day 186). Acidification (acidogenesis and acetogenesis) was dominant in LR2 over the first four weeks (Days 187-216); as was evident from the greater extent of pH decrease (7.83 to 6.15) resulting from VFA production. The lower pH resulting from acidification generally enhances metal solubility, and metal leaching from MSW was expected [25], which was observed for Zn, Cu, Cd, Pb and Ni (refer to section 3.2). This was followed by approximately seven weeks of methanogenesis (Days 217-263); as indicated by a rapid acceleration in methane production rate up to 50 m^3 CH_4 h^{-1}, a gradual increase in pH (to 8.09) and depletion of VFAs.

Although the sCOD removal efficiency was ~93%, the stabilised leachate still contained a high residual sCOD content (~5.6 g/l). This recalcitrant DOM most likely consisted of humic compounds such as humic and fulvic acids [26]. The recalcitrant DOM appeared similar in both reactors. The effect of metal complexation with dissolved organic matter is discussed in section 3.5.

Ammonium-N increased from 2.3g/l to an average of ~3.0 g/l with the sequential batch digestion, which are at the lower end of the reported inhibitory range from 1.7 to 14 g/l [27]. Ammonium-N concentrations that inhibit methanogenesis vary due to differences in substrates, inocula, environmental conditions (e.g. temperature, pH), and acclimation periods [28]. Based on the corresponding increase in biogas

production rates and the average methane yield of 123 ± 15 m^3 per tonnes of dry waste (equal to 95% of the long term biochemical methane potential yield), it is unlikely that ammonium-N caused any significant inhibition in this study.

3.2 Heavy metal profiles in the leachate

The greatest pH fluctuation (6.15-8.19) occurred in the leachate from LR2. Therefore, we focused on the fluctuation of dissolved heavy metal concentrations over these 104 days. Heavy metal concentrations in the leachate from the two landfill reactors during the entire digestion period are illustrated in the box plot in Fig. 2 and Table 2. Ranges of all metal levels were within the published values (Table 2), except for Pb [3, 15, 17]. Varying metal concentrations have been reported in landfill leachate studies [3, 15]. Generally, Zn content in the MSW is higher than other metals such as Cu [29]. The current study had a relatively higher Pb concentration. MSW disposed in landfills may also include lead-containing waste, such as old computer monitors or defunct analogue television sets containing cathode ray tubes [30].

The profiles of the metal concentrations in leachate during the operation of landfill bioreactors are shown in Fig. 3. During the sequential flooding and draining regime (Day 187 - Day 290), Zn, Cu and Pb concentrations peaked in both reactors in response to acidification (Day 187 - Day 216). This phenomenon also occurred with Cd and Ni in LR2 during the same time period. However, the Ni concentration in LR1 appeared unaffected. Cadmium was below the detection limit in LR1 during the entire digestion. Furthermore, Cr concentrations appeared to decline in response to the increased acidity, opposite to the generally-observed pH response. All metal concentrations stabilised towards the end of anaerobic digestion (when the biogas

production rate declined rapidly) except for As, which fluctuated erratically between 0.05 and 0.15 mg/l. Zinc was the most prevalent dissolved heavy metal and reached a maximum of 10.5 mg/l, followed by Pb (3.5 mg/l), Ni (1.2 mg/l) and Cu (0.8 mg/l). Lo et al. [23] reported similar Cr and Ni solubilities in metal-containing MSW leachate ranging from pH 6 to 8. Furthermore, the authors observed amphoteric properties (Cu, Zn, Pb and Cd), where solubility increased when the pH became extreme acidic (pH 1) or basic (pH 13) - presumably as metal salts dissolved.

3.3 Simulation of dissolution and precipitation using selected metal salts

The difference (in orders of magnitude) between the PHREEQC simulated and measured dissolved heavy metal concentrations in LR2 are presented in Table 3. The simulations for metal concentrations at equilibrium showed a similar trend with regard to metal concentrations in response to varied pH. There was a minor increase of solubilised metals when the pH deceased from alkaline (pH 7.8) to neutral conditions, and a major increase in metal concentrations when pH changed from neutral to acidic (pH 6.1). For selected equilibria with metal hydroxide and metal carbonate salts, the simulated concentrations were much higher than the experimental data for all assigned pH values, while all simulated concentrations were much lower for equilibria with the respective sulphide salt. In the presence of sufficient sulphate these bacteria generate H_2S (present as HS^- or S^{2-} depending on pH), which precipitates metal ions as metal sulphides that have very low solubility coefficients. As sulphide precipitation occurs relatively quickly (<24 h), the high dissolved heavy metal concentrations are likely due to either unaccounted complexation or insufficient sulphate/sulphide in the leachate, rather than kinetic limitations to attaining equilibria [10]. The overestimation of PHREEQC simulation when using metal hydroxide and

metal carbonate as the mineralogical phases suggests HS^- impacted on all dissolved metals. The minor effect of sulphur on Cr precipitation was reported by Möller et al. [10], who studied the impact of SRB on the removal of heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb and Zn from landfill leachate in a packed bed process, with Cd and Cu being removed by SRB most efficiently.

All metal concentrations were static prior to sequencing the two landfill reactors on Day 187. At this stage the mineral phases were more than likely in equilibrium as dissolved metal concentrations were static for a prolonged period prior to the sequential flooding and draining of LR2 (Fig. 3). The Cr simulation demonstrated the reverse of the pattern displayed by other metals (e.g., Zn, Cu or Pb) at acidic condition or slightly alkaline condition.

The VFAs, expressed in PHREEQC as acetic acid, displayed no major effect on the simulation results, and a more complex choice of DOM could potentially have improved the simulated data. The finding that the leaching of heavy metals was not controlled by solubility constraints indicated that the heavy metal concentrations were not high enough to initiate either carbonate or hydroxide precipitation at the pH levels observed in the bioreactors. The increasing concentrations for most heavy metals at the start of sequential flood and drain regime indicates that the combination of degraded MSW (releasing adsorbed metals) and acidification (lowering the pH and protonating the negatively charged functional groups in the surface of MSW sorbents) might be the primary cause of metal desorption from the particulates [31]. Towards the end of the digestion the VFA content in the leachate was negligible (e.g., Day 146-186 for LR1 and Day 270-290 for LR2). However, the remaining recalcitrant DOM in

the leachate might contribute to the higher metals' measurements (i.e., heavy metal-DOM complexation) at lower free metal activities under slightly alkaline conditions [32].

3.4 Effect of metal adsorption to particulate matter

Adsorption is one process that could strongly impact on dissolved metal concentrations in the leachate. The mobility of heavy metals in leachate can be affected by adsorption to particulate matter (e.g., food, cardboard, paper, rubber, plastic, etc.) in MSW at different pH conditions, thus reducing the dissolved metal concentrations, as illustrated in Fig. 4. Food waste was one of the key components in shredded MSW used in this study. Fruit waste is an excellent sorbents for heavy metal removal due to its large surface area, high swelling capacity and good mechanical strength [33, 34]. Waste paper and cardboard (another major component of OFMSW) is also an efficient metals adsorbent. It is used as a low-cost waste material to remove heavy metal from mine wastewater [35].

A sufficient hydraulic retention time in landfill reactors allow the metal adsorption process to reach equilibrium. Correlations of pH with metal concentrations from onset of the sequential flood and drain regime to the end of digestion (Day 188-260) are shown in Fig. 5. Dissolved Zn, Cu, Cd, Pb and Ni concentrations decreased as the pH increased. This phenomenon is in agreement with that reported by Annadurai et al. [33] who found a greater metal adsorption (Zn, Cu, Pb Co and Ni) to banana and orange waste occurred at a higher pH, and plateaued at pH of between 7.5 and 8. The positive relationship of pH and adsorption to MSW was further demonstrated by Lo et al.[23], who investigated the distribution of six heavy metals (Zn, Cu, Ni, Pb, Cd, and

Cr at 10 mg/l) in MSW with varying pH. The authors observed (1) adsorption increased with an increase of pH from 6 to 9 (except Ni and Pb), (2) soluble metal ion concentrations were highest in the order of Ni>Cu>Cr>Zn>Cd>Pb in MSW leachate between pH 8 to 12; and (3) Cu, Zn, Pb and Cd possessed amphibious properties. However, in the current study no amphoteric solubility properties were observed in response to the variation of pH between 6 and 8.

Statistical analysis (ANOVA) demonstrated a significant negative relationship between pH and most dissolved metal concentrations (P<0.01), indicating metal adsorption to particulate matter is the dominant process. However, a weak R^2 (<0.2) for dissolved As and Co indicates a very poor relationship with pH (P<0.05). This suggests that adsorption between metals and the solid components of shredded MSW, and complexation between metals and soluble organic components in leachate co-exist during AD. Depending on the speciation of metals under a specific condition, metals are absorbed into particles competitively, and some metals with low affinity to particle surfaces might form metal-DOM complex with a specific stability constants subjected to the denticity (active donor groups that can bind to heavy metal cations) of the DOM ligands. The reaction may be reversed by competitive metals binding to DOM, while some metals with low DOM affinities may (1) remain in the solution, or (2) adsorb onto solid particles. Alternatively, the metal-DOM complex may also absorb onto particles [36]. In this study As and Co are possibly distributed between the solid surface phase (adsorption) and the liquid solution (metal-DOM complex) irregularly due to the weak competitiveness of both processes.

3.5 Effect of metal complexation with dissolved organic matter

The solubility of heavy metals in landfill leachate is affected by the concentrations of DOM, which is typically given in terms of a surrogate measurement: soluble chemical oxygen demand (sCOD). Low molecular weight organic compounds that make up the sCOD (e.g., polyphenols, simple aliphatic acids, amino acids and sugar acids) can form soluble complexes with heavy metals, which prevent metals adsorbing or complexing to the solid phase in MSW, thereby increasing dissolved metal concentrations as metal-DOM complexes [37]. In the current study, the sCOD of the leachate varied greatly (5 to 90 g/l). Although speculative, it is highly probable that components of this DOM contributed to greater overall solubility of heavy metals in the leachate. For example, Antoniadis and Alloway [38] demonstrated this effect with Cd, Ni and Zn, where extractability from soils increased significantly in the presence of natural dissolved organic compounds.

In this study, simulation of dissolution and precipitation using selected metal salts observed a counter-intuitive pattern of Cr fluctuation in the leachate (Fig. 3). Here, significant complexing of free Cr species with DOM should be considered (Fig. 4), as DOM-complexed metals comprise a wide range (0-98%) of the dissolved metals in solution [32]. A study by Gustafsson et al. [22] presented a pattern of dissolved Cr concentration as a function of pH in the soil suspensions, which is in agreement with our findings in the study. The authors assumed that Cr(III) forms two DOM complexes: one monomeric complex $(RO)_2Cr^+$ bound bidentately to DOM, and one dimeric complex $(RO)_3Cr_2(OH)_2^+$ - each with a specific Stockholm Humic Model equilibrium constant. The authors presented Cr(III) speciation as a function of pH in the soil suspensions, in which a higher pH (pH >5) lowered the adsorption capacity of both Cr(III)-DOM complexes with particulate matter, increased the dissolved dimeric

complex Cr(III), i.e., polynuclear Cr(III)-Suwannee River Fulvic Acid complexes, which is suggested as an important Cr species in many environments.

Further research on the simulation of metal-DOM complexation during the entire course of anaerobic digestion of MSW should be performed. The complex effects of metal-DOM complexation on metal solubility and distribution should consider: (1) various metal oxidation states; (2) various unknown organic and inorganic ligands present in the liquid matrix; (3) prevalent metals (e.g. Ca^{2+} and Mg^{2+}) out-competing heavy metals for DOM binding sites; and (4) the low solubility and potential formation of intrinsic metal colloids and nanoclusters [39, 40].

4. Conclusions

The study profiled the fluctuating heavy metal concentrations in leachate during anaerobic digestion of shredded MSW in landfill bioreactors (1000 tonnes per reactor) homogenised by the flood and drain process. pH played an important role in distribution and interactions of the dissolved heavy metals in leachate. The study demonstrated that the pH variation in leachate caused mainly by the accumulation and consumption of volatile fatty acids during AD of shredded MSW governed various processes, including dissolution and precipitation of various metal mineralogical phases. In addition, metal complexation with DOM and metal adsorption to MSW are important physical, chemical and biological processes affecting dissolved metal concentration in the leachate. Metal adsorption to MSW may result in the higher dissolved metal concentrations at the lower pH due to the electrostatic interaction at the complex MSW surface. Strong negative correlations were observed between pH

and Zn, Cu, Ni, Pb and Cd, indicating that adsorption to solid materials was the dominant process. A strong positive correlation between pH and Cr indicated that complexation with dissolved organic matter was the dominant process here. Chromium complexation with DOM resulted in lower dissolved concentrations at the lower pH due to decreased dissolution of Cr(III)-DOM complexes. Both processes (adsorption and complexation) might contribute to metal distributions for As and Co, as they displayed a weak correlation to pH and As and Co. Data from this study indicates the possibility of correlating certain dissolved heavy metal concentrations to specific anaerobic degradation stages.

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Figure Captions

Figure 1: Leachate properties: pH, NH_4^+-N, total VFA and soluble COD (◇ LR1 Eff, □ LR2 Eff).

Figure 2: Box plots of heavy metal concentrations in leachate during the entire digestion for the two landfill reactors.

Figure 3: Profiles of heavy metals in the leachate from the two landfill reactors (◇ LR1 Eff, □ LR2 Eff).

Figure 4: Proposed mechanism of heavy metal distribution in landfill reactors.

Figure 5: Correlation of pH with dissolved metal concentrations from onset of the sequential flood and drain regime to the end of digestion in both reactors.

Figure 1

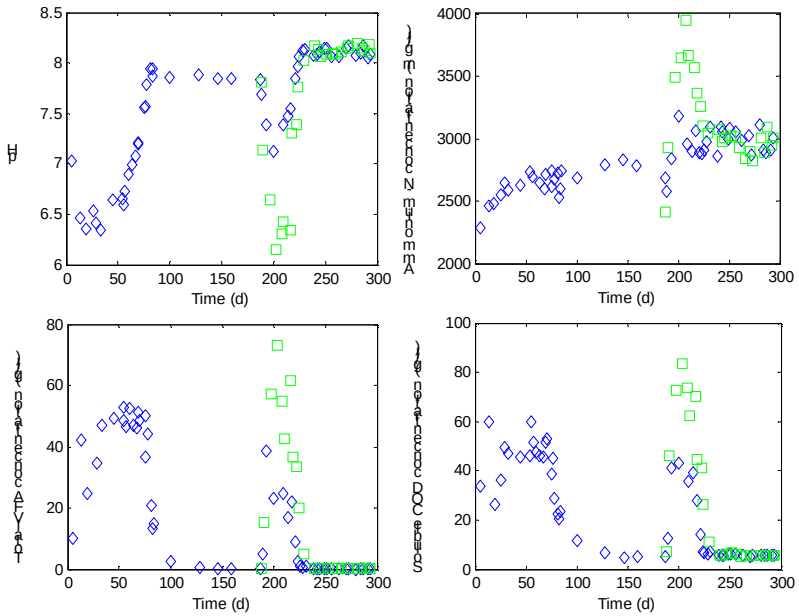

Figure 2

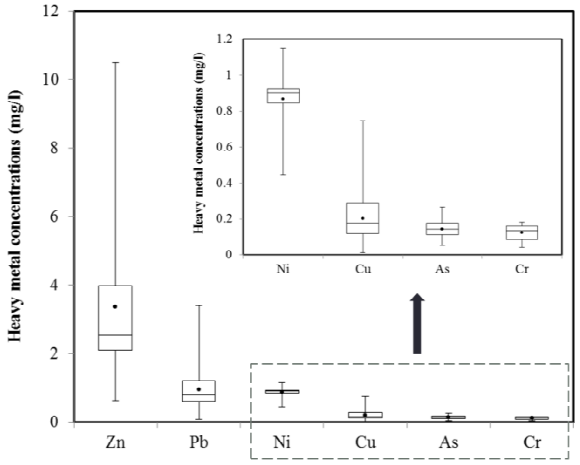

Figure 3

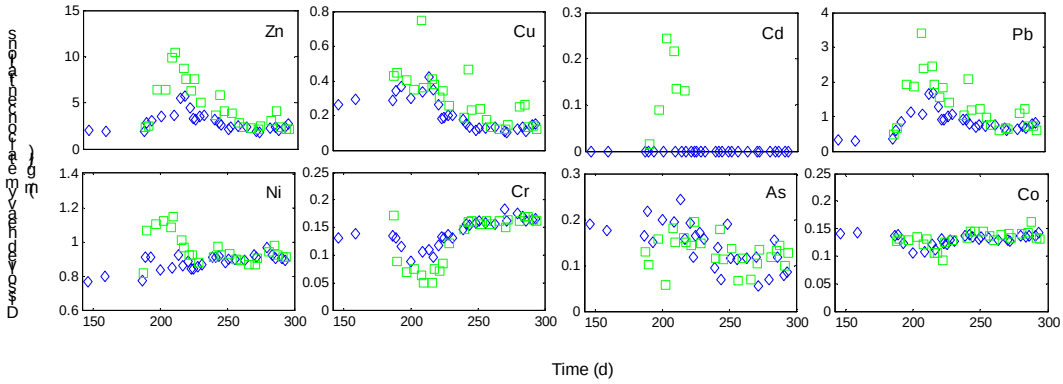

Figure 4

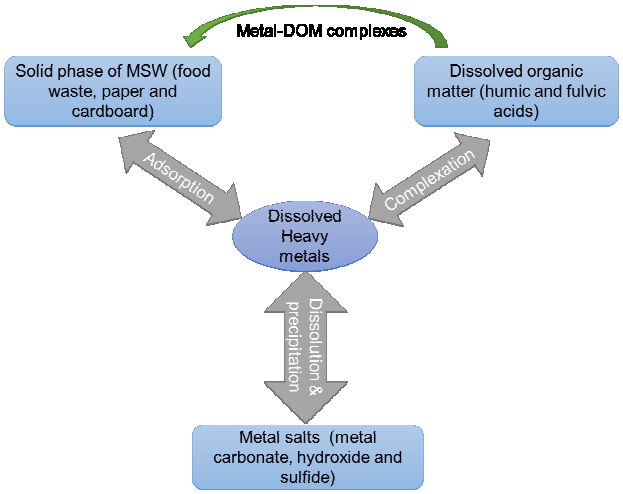

Figure 5

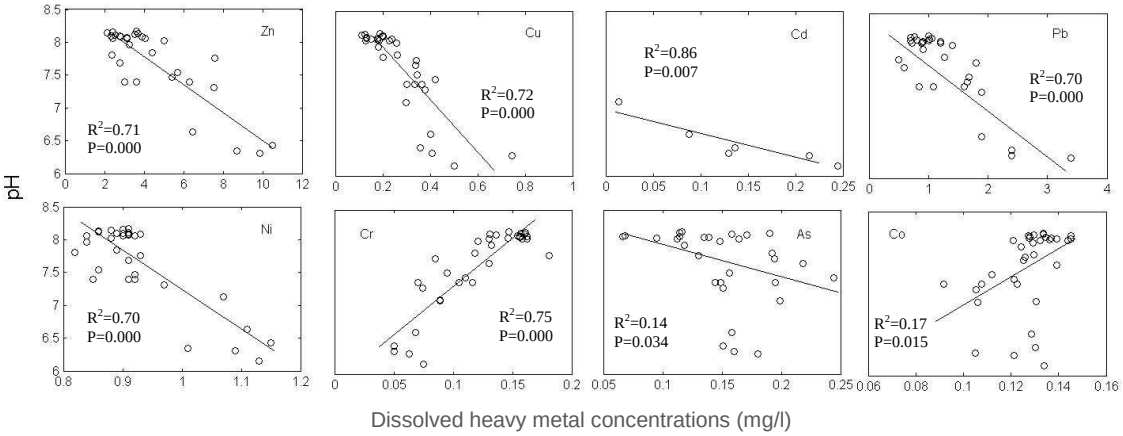

Table 1 Characteristics of la cement of

the sequential flood and drain regime of LR2.

Leachate characteristics	Landfill bioreactor leachate*
pH	7.82 ± 0.01
Temperature (°C)	36.2 ± 0.1
sCOD	5300 ± 70
Dissolved inorganic carbon	816 ± 32
VFAs	156 ± 13
Ammonium	2685 ± 101
Aluminium	3.89 ± 0.43
Calcium	67.3 ± 4.4
Chloride	ND**
Iron	8.64 ± 0.25
Magnesium	272.8 ± 15.7
Potassium	2075 ± 7
Phosphate	42.9 ± 2.0
Sodium	3927 ± 32
Sulfur	72.8 ± 2.7
Zinc	1.87 ± 0.06
Copper	0.28 ± 0.01
Lead	0.41 ± 0.06
Nickle	0.78 ± 0.02
Arsenic	0.11 ± 0.03
Cadmium	0.00 ± 0.00
Cobalt	0.14 ± 0.02
Chromium	0.13 ± 0.02

* All values are in mg/l expect for pH and where indicated
** Chloride concentration is subjected to charge balance for the modelling purpose.

Table 2 Comparison of the range of dissolved heavy metal concentrations in leachate

Heavy metals	MCL*	Current study**	Barlaz et al., 2010	Baun & Christensen, 2004
Zinc	0.8	0.64 - 10.49	0 - 112	0.01 - 155
Copper	0.25	0.01 - 0.75	0.003 - 0.49	0.0005 - 1.4
Lead	0.006	0.09 - 3.40	0 - 0.3	0.0005 - 1.5
Nickle	0.20	0.30 - 1.15	-	0.001 - 3.2
Arsenic	0.05	0.06 - 0.27	0.005 - 0.155	0.0005 - 1.6
Cadmium	0.01	ND - 0.24	0 - 0.419	0.00002 - 0.13
Cobalt	-	0.05 - 0.16	-	0.001 - 0.95
Chromium	0.05	0.04 - 0.18	0 - 1.98	0.0005 - 1.6

* Maximum Contaminant Levels
** All values are in mg/l

Table 3 Difference (in orders of magnitude) between the simulated PHREEQC data and the measured dissolved heavy metal concentrations in LR2.

	Mineral phase

Heavy metals	Metal hydroxide	Metal carbonate	Metal sulphide
Zn	+4*	+1	-3**
Cu	+3	+2	-4
Pb	+3	+2	-3
Ni	+4	+2	-4
As	NA***	NA	NA
Cd	+3	+2	NA
Co	NA	+3	NA
Cr	+2	NA	NA

*Positive number (e.g., +4) denotes that the simulation results are four orders of magnitude higher than the measured results.

**Negative number (e.g., -3) denotes that the simulation results are three orders of magnitude lower than the measured results.

*** NA (not applicable) denotes the lack of information in the database.